Mechanism for formation of NaBH$_4$ proposed as low-pressure process for storing hydrogen in borosilicate glass–sodium solid system: a hydrogen storage material

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Abstract. The mechanism for the formation of sodium borohydride (NaBH$_4$) was investigated for its ability to store hydrogen in the borosilicate glass–sodium (BSG–Na) solid system under low hydrogen pressure. BSG, which was prepared by melting borax with silica, was used as the starting material in the BSG–Na system that would be prepared to store hydrogen. It was observed that the mechanism for storing hydrogen in the BSG–Na solid system consisted of six steps and when the BSG–Na system was heated under a pressure of 4 atm, which was created through the use of hydrogen atmosphere, the storage of hydrogen occurred at nearly 480°C for approximate duration of 200 min, with the excellent yield (97%). In addition, the hydrogen storage capacity of the NaBH$_4$ sample was measured using the Au–PS structure, which was designed as a mini-hydrogen cell. It was determined that the minimum amount of NaBH$_4$ to generate the maximum volume of hydrogen gas was 12 mg/ml at 270 mV.

Keywords. Materials for storage of hydrogen; sodium borohydride; borosilicate glass; mechanism of formation.

1. Introduction

Currently, energy storage is becoming an increasingly important concern among the global energy system. It is desirable to identify an ideal energy carrier, which embodies unique characteristics such as high capacity for energy storage, safety and environmental friendliness. In recent years, hydrogen is being considered as an interesting alternative to be an excellent energy carrier (Veziroglu 1997). Hydrogen is produced from fossil fuels (C_xH_y) through the use of a variety of process technologies including steam reforming, partial oxidation, auto-thermal reforming and through various processes that make use of water such as water electrolysis, photo-electrolysis, photo-biological production and high-temperature decomposition. Hydrogen can be stored in tanks in compressed gaseous form in order to be used for large scale applications, in liquid form for space technology and high-energy nuclear physics research, or in the form of chemical hydrides in order to be used in the transportation sector (Riss *et al* 2006). Traditional hydrogen storage technology was limited because of the hazard risk it imposes during storage and transportation and hydrogen is a light gas that takes up a considerable amount of space. These difficulties are the main problems of using hydrogen on vehicular applications (Dincer 2002; Sherif *et al* 2003). It was suggested that NaBH$_4$ can be used as an anodic fuel in a fuel cell or as a hydrogen storage medium to overcome these problems. NaBH$_4$ contains 10·6 wt% hydrogen, which is far more than the amount that other chemical hydrides contain (Schlinger *et al* 1953; Kim *et al* 2004).

When NaBH$_4$ dissolves in water or in an alkaline solution, in the presence of a catalyst, it releases its hydrogen and metaborate (NaBO$_2$) is formed as a by-product:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 \cdot xH_2O\,(aq) + 4H_2$$
$$+\ \text{heat}\ (x = 2\ \text{or}\ 4) \tag{1}$$
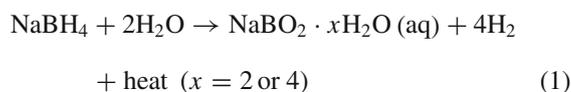
Hydrolysis reaction occurs at different rates depending on the properties of the catalyst (Levy *et al* 1960). Amendola *et al* (2000) studied Ru-based catalysts for the generation of H$_2$. Kojima *et al* (2002) reported that metal oxides were useful as catalysts and selected PtLiCoO$_2$ as the most suitable catalyst for controlling the generation of H$_2$ from NaBH$_4$. Moreover, the hydrolysis of NaBH$_4$ using a non-noble nickel-based catalyst was studied in batch reactors. It was suggested that the catalyst was capable of being used in practical applications such as hydrogen generator coupled with fuel cells (Pinto *et al* 2006). Co-B catalyst was also reported for its high capability for hydrogen generation (Lee *et al* 2007).

NaBH$_4$ is a non-reversible chemical hydride that was used in the hydrolysis and the generation of H$_2$. Therefore, various techniques for the production of NaBH$_4$ and the recycling of NaBO$_2$ were proposed. Cooper (1973) suggested the electrochemical conversion of NaBO$_2$ at room temperature. They concluded that borate ions from NaBO$_2$ were reduced to

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borohydride ions in the electrolytic cell having the cationic-selective membrane separating the anode and the cathode compartments. Hale describes an electrolytical cell for the production of $NaBH_4$, which comprises of an anode compartment containing a solution of aqueous sulfuric acid and a 25% solution of tetramethlyammonium borate used as the catholyte adjacent to the cathode compartment. The anode and the cathode compartments were separated by means of a cationic membrane made of Nafion[427] (Hale and Sharifian 1990). Kojima and Haga (2003) determined that $NaBH_4$ was synthesized by annealing a mixture of $NaBO_2$ with MgH_2 or $NaBO_2$ with Mg_2Si under high H_2 pressure. Also, it was considered that coke or methane could be used in the recycling of $NaBO_2$ back to $NaBH_4$. Li *et al* (2003) reported the presence of a reaction of metaborate with MgH_2 through ball milling at room temperature. Additionally, the mechanism of $NaBH_4$ formation through the reaction of $NaBO_2$ with Mg and H_2 was also studied (Li *et al* 2007). Park *et al* (2007) reported a new electrochemical method for the recycling of $NaBO_2$ back to $NaBH_4$. The recycling of $NaBO_2$ to $NaBH_4$ took place as a two-step process, involving electrochemical and thermal treatment routes.

$NaBH_4$ is commonly produced from sodium hydride and methyl borate using a process, which was invented by Schlinger *et al* (1953);

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3. \quad (2)$$

Li *et al* (2003a, b) studied the production of $NaBH_4$ through the reaction of borax and MgH_2 by ball milling at room temperature;

$$NaBO_2 + MgH_2 \rightarrow NaBH_4 + MgO. \quad (3)$$
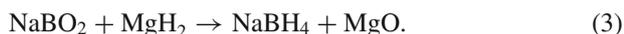
Beside these methods, boron minerals such as borax, ulexite and colemanite were used as sources of boron in thermo-chemical reactions under hydrogen atmosphere for the synthesis of $NaBH_4$. In our previous study, we have reported a high pressure process (HPP) for producing $NaBH_4$, which was based on the conversion reaction of borosilicate glass at a temperature of 475°C under hydrogen pressure of 22 atm for a duration of 70 min. $NaBH_4$ was produced by this simple and easy method, which had a very high production yield, obtained at a short reaction time (Kantürk and Pişkin 2007).

There are no detailed studies on the storage of hydrogen in the borosilicate glass–sodium (BSG–Na) system that was conducted under low hydrogen pressure and on the mechanism of $NaBH_4$ formation. In this study, we present an investigation of hydrogen storage in the BSG-Na solid system that was conducted under low hydrogen pressure based on a thermo-chemical reaction in which sodium borohydride ($NaBH_4$) was formed. The hydrogen storage mechanism occurring in the BSG-Na solid system and the mechanism of $NaBH_4$ formation were studied through the hydrogen consumption behaviour that was observed during the reaction.

2. Experimental

2.1 *Characterization of crystalline structure: X-ray diffraction (XRD) analysis*

Crystalline structures of the materials were determined by X-Ray powder diffraction (XRD) technique. The X-ray analyses were carried out at ambient temperature using Philips Panalytical X'Pert-Pro diffractometer with CuKα radiation ($\lambda = 0.15418$ mm) at operating parameters of 40 mA and 45 kV (with step size of 0.02° and speed of 1°/min). The acquired XRD patterns were compared with the powder diffraction files (PDF) in order to identify the crystalline phase. 01-074-1891 and 00-016-0818 PDF files were used to index $NaBH_4$ and Na_2SiO_3, respectively. Characteristic peaks of the standard with the reflection lines ($h \quad k \quad l$) are provided in table 1.

2.2 *Experimental procedure for the low-pressure storage process of hydrogen in the BSG–Na system: NaBH$_4$ formation*

Storage of hydrogen in the BSG–Na system under low-hydrogen pressure occurs as dictated by the following thermo-chemical reaction (Schubert *et al* 1963);

$$BSG–Na + 8H_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3. \quad (4)$$

Based on reaction chemistry, when hydrogen gas was to be stored in the BSG–Na system, $NaBH_4$ forms and is used for the storage of hydrogen. The experimental procedure to obtain this result consists of the following four key steps: (i) Preparation of BSG as a starting material, (ii) storage of hydrogen in the BSG-Na system and formation of $NaBH_4$, (iii) determination of hydrogen storage capacity and (iv) investigation of the mechanism for the storage of hydrogen and the formation of $NaBH_4$.

2.2a *Preparation of BSG as a starting material*: Borosilicate glass (BSG) was used as a starting material in the

Table 1. Crystallographic peaks of $NaBH_4$ and Na_2SiO_3 in standard PDF cards.

Reference material	PDF number	h k l	d(Å)	2θ (°)
Sodium borohydride ($NaBH_4$)	01-074-1891	2 0 0	3.08175	28.950
		2 2 0	2.17913	41.402
		1 1 1	3.55850	25.003
Sodium silicate (Na_2SiO_3)	00-016-0818	1 1 1	3.04000	29.356
		0 0 2	2.41200	37.249
		1 1 1	2.57000	34.882

Table 2. Chemical composition (%) of the borosilicate glass prepared.

Constituents		Concentration (%)
Major	SiO_2	69·376
	B_2O_3	20·278
	Na_2O	9·687
Minor	Al_2O_3	0·362
	P_2O_5	0·023
	SO_3	0·013
	K_2O	0·117
	CaO	0·082
	TiO_2	0·004
	MnO	0·015
	Fe_2O_3	0·020
	ZnO	0·009
	ZrO_2	0·013

Figure 1. FT–IR spectra of borosilicate glass.

low-pressure process. BSG was prepared using borax ($Na_2B_4O_7$), supplied from Bandırma Eti Mine Works—Turkey and quartz (SiO_2) (Fluka, 99% purity). The components were mixed together and melted in a refractory pot in an electrically heated furnace at 1300°C. The melt was frequently stirred to ensure good homogeneity. After it was completely liquefied, the melt was poured into water and allowed to cool down to room temperature. The cast glass was crushed, pulverized and sieved to obtain particles of size below 150 μm. The sample was dried at 105°C in an oven overnight and stored under inert atmosphere until use. The composition of the prepared BSG is given in table 2. The chemical composition analysis of this sample was carried out by wavelength-dispersive X-Ray fluorescence spectroscopy (XRF). In order to reduce the particle size variation, the sample was ground in a disc mill and the powder was pressed into pellets under 20 t. The pressed pellet was placed into the standard sample holder and subsequently loaded into the XRF spectrometer (Axios, PANalytical).

Infrared absorption spectrum of the BSG was acquired using a Fourier-transform infrared spectrometer (Perkin Elmer Spectrum One) equipped with DTGS detector and the spectra was recorded at room temperature using the KBr technique. The sample, in the form of a KBr pellet (1:100), was obtained by being pressed under 10 t. The IR spectrum was recorded in the spectral range of 4000–400 cm^{-1} at a resolution of 8 cm^{-1}. The FT-IR spectra of BSG exhibited the infrared absorption band as shown in figure 1. The prominent peaks were at 3432·75 cm^{-1} (–OH), 1424·59 cm^{-1} (B–O), 1073·05 cm^{-1} (Si–O), 798·40 cm^{-1} (O–Si–O), 707·87 cm^{-1} (B–O) and 475·75 cm^{-1} (Si–O–Si).

2.2b *Storage of hydrogen in the BSG–Na system and the formation of NaBH₄*: The low-pressure process diagram is shown in figure 2. The experiment was carried out in a stainless-steel autoclave which was equipped with a mechanical stirrer and a serpentine that allows water cooling. It was
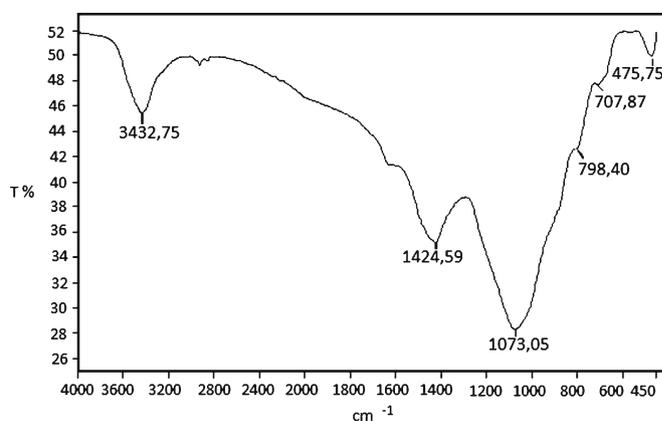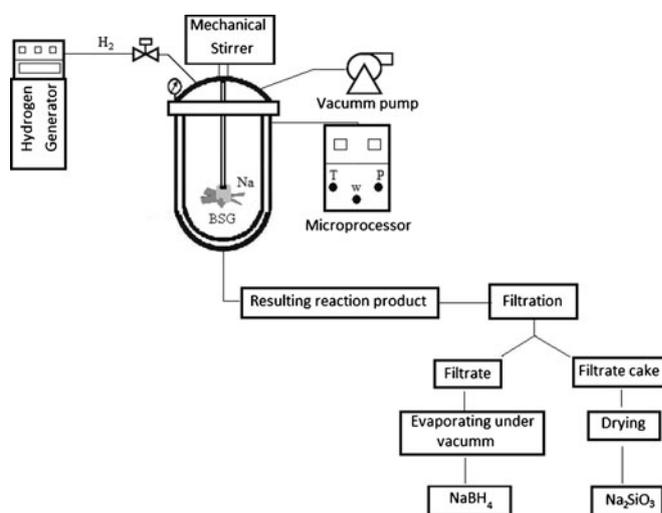
Figure 2. Process diagram of low pressure process.

designed for a maximum pressure of 50 atm and a maximum operating temperature of 550°C. The control of temperature and pressure is achieved automatically via the microprocessor based PID controller. The autoclave is connected to a hydrogen generator (Claind HG 2600), which is an alternative to high pressure gas cylinders and which includes a unique microprocessor control continuously monitoring all operation parameters. Hydrogen gas of 99·99% purity is produced in a copper-nickel electrolytic cell through the electrolysis of demineralized water. Hydrogen flow rate was set to 600 ml/min at its maximum.

BSG–Na system (in 1:16 mole ratio) was introduced into the autoclave, which was evacuated by a vacuum pump for 30 min in order to remove the air and the moisture prior to the charging of the hydrogen gas into the chamber. Pure hydrogen gas was continuously fed and the autoclave was heated. Hydrogen was kept at a constant pressure of 4 atm during the reaction and this was controlled by the microprocessor of the hydrogen generator. The saturation of the BSG–Na system
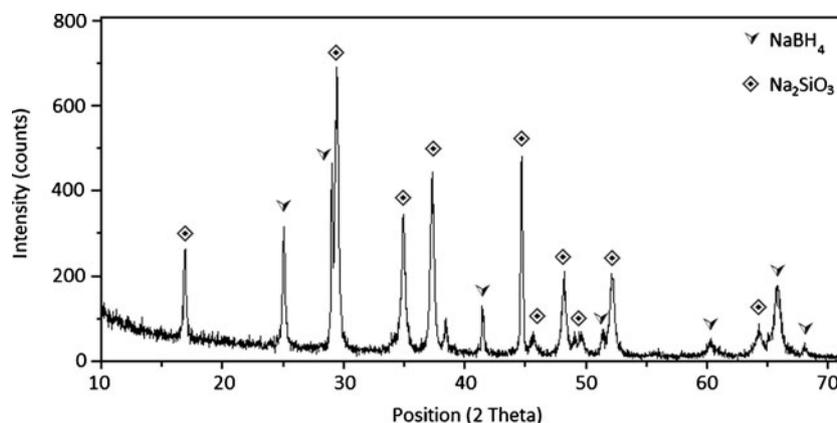
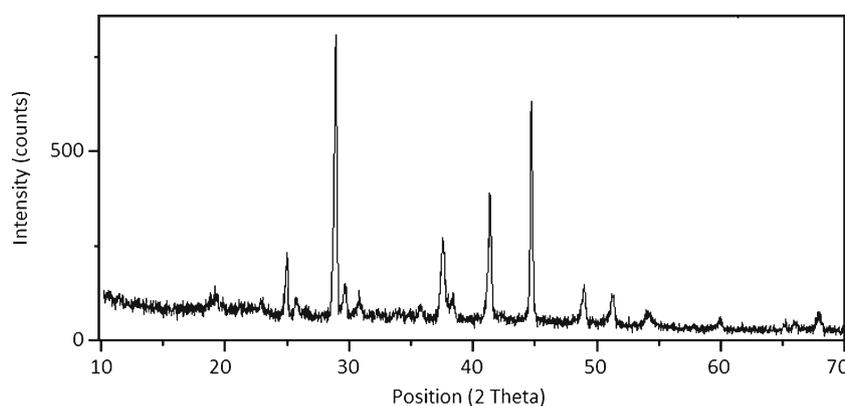**Figure 3.** XRD pattern of resulting reaction product (NaBH$_4$, Na$_2$SiO$_3$).

Figure 4. XRD pattern of main product (NaBH$_4$).

with hydrogen was determined based on the consumption characteristic of hydrogen as it was taken up by BSG–Na. The heating system of the autoclave was shut down when further hydrogen uptake ceased to occur and the reaction mixture was allowed to cool down to the ambient temperature under the hydrogen atmosphere.

The resulting reaction product was analysed using the XRD technique for the identification of NaBH$_4$ formation and the XRD pattern is given in figure 3. The solid–liquid extraction of NaBH$_4$ in the resulting reaction product was carried out. Filter paper was used to separate the extraction solution from the by-product and the remaining reactants. Following this step, the liquid solution was evaporated in a rotary evaporator and the obtained solid material (white powder) was analysed by the XRD technique and the obtained XRD pattern is given in figure 4. The filter cake that was acquired as the by-product was dried at 105°C for 2 h in a vacuum oven prior to its analysis by XRD (figure 5).

2.2c *Determination of hydrogen storage capacity*: The hydrogen storage capacity of the NaBH$_4$ sample was measured using the Au–PS structure, which is designed as a mini-hydrogen cell. This cell is only sensitive to hydrogen gas and can be described as acting like a hydrogen sensor. The Au–PS structure has been prepared by the deposition of Au film onto the PS surface at room temperature using the electron-beam evaporation technique (Dzhafarov *et al* 2004). Hydrogen gas, which is generated by the hydrolysis of NaBH$_4$, has been released during the generation of open-circuit voltage (V_{oc}) in the Au–PS interface. V_{oc} characteristic of the NaBH$_4$ solution in the Au–PS structure was examined in order to determine the minimum amount of NaBH$_4$ to generate the maximum volume of hydrogen gas. V_{oc} values at different NaBH$_4$ concentrations (30, 20, 15, 12 and 10 mg/ml) were collected using a voltmeter in the measuring cell. The obtained V_{oc} data of the produced NaBH$_4$ were plotted against the concentrations as shown in figure 6. A similar study was also conducted using commercial NaBH$_4$ (Riedel de Haen, 96%) under the same conditions and the value was determined as 210 mV at 15 mg/ml concentration.

2.2d *Investigation of the storage mechanism of hydrogen and the formation mechanism of NaBH$_4$*: The storage mechanism of hydrogen and the formation mechanism of

NaBH$_4$ in the BSG–Na system were examined through the consumption characteristics of hydrogen. Temperature and H$_2$ pressure variations inside the autoclave were monitored as a function of the reaction time by taking periodic readings on the microprocessor. Data were plotted against the reaction temperature and time as shown in figure 7.

3. Results and discussion

3.1 *X-ray diffraction analysis*

Figure 3 shows the outcome of the XRD analysis of the resulting reaction product after storing the hydrogen gas in the BSG–Na solid system. The X-ray pattern verified the existence of NaBH$_4$ and Na$_2$SiO$_3$. Characteristic peaks of NaBH$_4$ are observed for the diffraction angles of 28·97°, 41·42° and 24·98° (indexed with "$\vee$") in the spectrum obtained from the diffractometer. The XRD results indicate that the (2 0 0), (2 2 0) and (1 1 1) reflection lines, which are present in the standard pattern of NaBH$_4$ in the current powder diffraction file (PDF) database with accession number 01-074-1891, are all present in the XRD patterns of the currently obtained NaBH$_4$ sample. However, the diffraction peak positions at angles of 29·38°, 34·88° and 37·26° (indexed with "$\diamondsuit$") belong to the by-product; Na$_2$SiO$_3$.

Figure 4 displays qualitative analysis obtained from the XRD analysis of the main product after extraction, filtration and evaporation of the resulting reaction product. The XRD peaks clearly show the existence of NaBH$_4$. However, peaks belonging to Na$_2$SiO$_3$ were not apparent. NaBH$_4$ has cubic crystal structure with cell parameters of $a = b = c = 6·1635$ Å. The diffraction peak (2 0 0), corresponding to the diffraction angle of 28·95°, matched with the NaBH$_4$ characteristic peak.

Figure 5 illustrates the powder diffraction pattern of the by-product, which was obtained following the separation of NaBH$_4$ from the resulting reaction product. The XRD peaks demonstrate that the by-product was identified as Na$_2$SiO$_3$ (PDF number: 00-016-0818). The XRD analysis also showed that there was no diffraction peak belonging to NaBH$_4$.
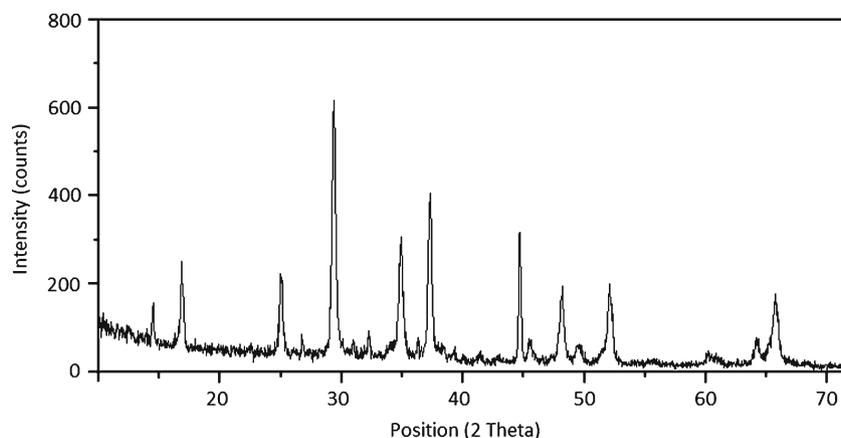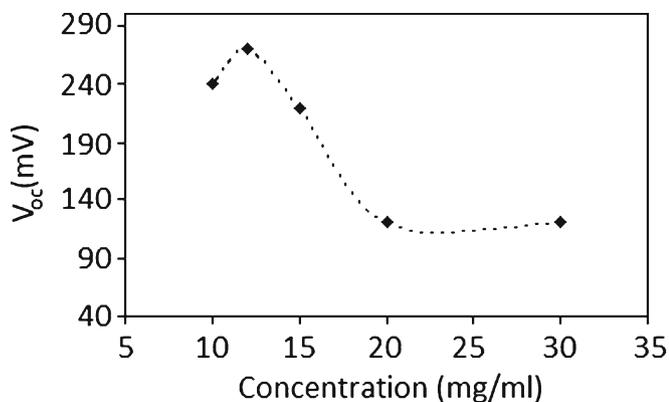

Figure 5. XRD pattern of byproduct (Na$_2$SiO$_3$).

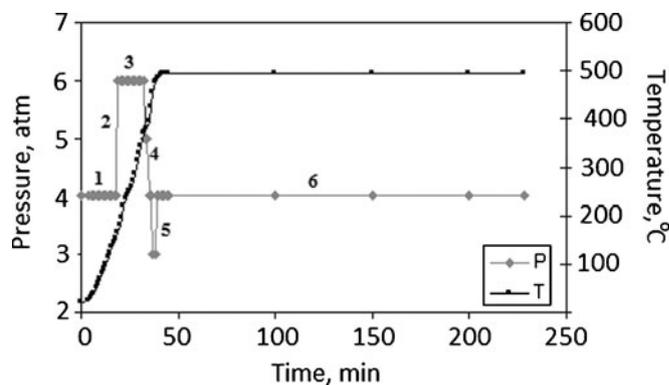**Figure 6.** V_{oc} data against the concentration of produced NaBH$_4$.

Figure 7. Mechanism of storing of hydrogen and mechanism of NaBH$_4$ formation.

Table 3. Reaction parameters of $NaBH_4$ formation by high- and low-pressure process.

		NaBH$_4$ production processes			
Process	Type	Pressure (atm)	Temperature (°C)	Time (min)	Yield (%)
HPP	Batch	22	475	70	97
LPP	Continuous	4	480	200	97

3.2 *Determination of hydrogen storage capacity*

Figure 6 provides the plot of the open-circuit voltage (V_{oc}) data against the concentration of the produced $NaBH_4$. As indicated by this plot, it was determined that the minimum amount of $NaBH_4$ to generate the maximum volume of hydrogen gas was 12 mg/ml. The open-circuit voltage (V_{oc}) generated in the Au–PS interface by the hydrolysis of $NaBH_4$ was 270 mV at a concentration of 12 mg/ml. It can be observed that there is no significant difference in the hydrogen storage capacity between the product and the commercial $NaBH_4$. It should be noted that $NaBH_4$ is very hygroscopic and it releases hydrogen under ambient conditions.

3.3 *Hydrogen storage and NaBH$_4$ formation mechanisms*

Figure 7 shows the variation of pressure and temperature with reaction time. As shown in the figure, the hydrogen storage mechanism and the $NaBH_4$ formation mechanism are formulated as indicated in the following steps:

Step 1: Heating the reactor using a microprocessor starting at 20°C under 4 atm of hydrogen pressure, reaching 155°C without any pressure change in comparison to the initial conditions.

Step 2: The hydrogen pressure of the system is increased up to 6 atm suddenly as a result of the heating.

Step 3: The hydrogen pressure was stable at this stage during heating. Obviously, there was no interaction between hydrogen and BSG–Na solid system at these conditions.

Step 4: The system displayed a significant decrease in hydrogen pressure (from 6 to 3 atm) while heating the reactor up to 475°C. This was considered as an indicator of the BSG–Na system to absorb hydrogen gas to form $NaBH_4$.

Step 5: The microprocessor of the reactor intervened at a temperature of 480°C and the reactor was fed with hydrogen gas in order to attain hydrogen pressure of 4 atm. The system pressure was brought back to the initial value.

Step 6: Following the process of heating, $NaBH_4$ formation took place at 480°C under hydrogen pressure of 4 atm. After 200 min the consumption of hydrogen by the BSG–Na system ceased to occur. The reaction time was determined as 200 min, for the accumulation of hydrogen in the BSG–Na system and the formation of $NaBH_4$.

The low-pressure process (LPP) is compared with the high-pressure process (HPP) in the context of reaction time, reaction yield and the mechanism leading to $NaBH_4$. The reaction parameters are listed in table 3. The main difference between a low- and a high-pressure process was the type of hydrogenation process. In the HPP, hydrogen gas at 22 atm pressure was introduced into the autoclave and the batch reactor was heated. The hydrogen pressure was increased up to 23 atm while the temperature was 285°C and a considerable decrease in hydrogen pressure down to 4 atm occurred as a result of the formation of $NaBH_4$. The reaction time during the conversion of BSG to $NaBH_4$ was determined as 70 min in this process. Whereas in the LPP, hydrogen gas was continuously fed from a hydrogen generator into the autoclave during the conversion reaction in which BSG–Na was the reactant and $NaBH_4$ was the product. Hydrogen pressure was adjusted at a constant value of 4 atm via the control by the microprocessor of the generator. Therefore, the hydrogen pressure of the system is low during the reaction and the process is thus named as 'low-pressure process'. Reaction time for the formation of $NaBH_4$ is determined as 200 min as indicated by the plot displaying the mechanism of $NaBH_4$ formation (figure 7).

Based on the experimental observations for the hydrogenation mechanism, it could be determined that the BSG with Na system has a different hydrogen consumption reaction time depending on the method of hydrogenation. It was observed that the reaction time decreased when the conversion reaction was carried out under high hydrogen pressure at the same range of reaction temperature.

4. Conclusions

The results obtained from the investigation of the low-pressure process for the storage of hydrogen in the BSG–Na system and the mechanisms for the formation of $NaBH_4$ lead to the following conclusions:

- The low-pressure process occurred in four main steps: Preparation of BSG as a starting material, storage of hydrogen in the BSG–Na system, determination of the hydrogen storage capacity, investigation of the hydrogen storage mechanism and the formation of $NaBH_4$.
- Borosilicate glass was prepared by melting borax and quartz at 1300°C. The highlight of this operation was

the pouring of the melt into water to ensure the formation of a very brittle type of glass that was suitable for grinding.

- Measured V_{oc} values were related to the hydrogen storage capacity of NaBH$_4$ and the hydrogen storage capacity was measured in the Au–PS structure, which was designed as a mini-hydrogen cell.
- It was observed that the mechanism for storing hydrogen and the mechanism of NaBH$_4$ formation consisted of six stages.
- The reaction time was determined as 200 min for the storage of hydrogen in the BSG–Na system and the formation of NaBH$_4$ under low hydrogen pressure at 4 atm.

The following points can be further emphasized from the direct comparison of high-pressure and low-pressure processes:

- It is proved that the formation of NaBH$_4$, which was based on storing hydrogen in BSG–Na system, occured at a temperature range of 400–500°C for both processes either under high or low hydrogen pressure.
- The NaBH$_4$ formation yield did not depend on the process of hydrogenation. The excellent yields (97%) were achieved under any hydrogen pressure.
- The NaBH$_4$ formation time depended on the process of hydrogenation. It was found that the reaction time was 70 min under high hydrogen pressure and 200 min under low hydrogen pressure.

In conclusion, a high-pressure process is recommended to achieve excellent yields in a short reaction time for the formation of NaBH$_4$ and for the storage of hydrogen in the BSG–Na system.

Acknowledgements

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